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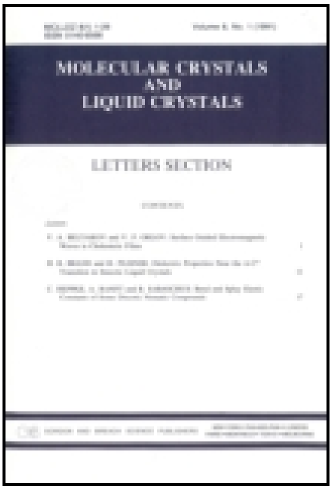

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

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Published online: 17 Nov 2014.

To cite this article: Jun Young Han & Chung Wung Bark (2014) Control of Optical Band Gap in La Doped Bismuth Titanate with Two Stage Doping, Molecular Crystals and Liquid Crystals, 597:1, 37-44, DOI: 10.1080/15421406.2014.931786

To link to this article: http://dx.doi.org/10.1080/15421406.2014.931786

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Mol. Cryst. Liq. Cryst., Vol. 597: pp. 37–44, 2014

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2014.931786

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Control of Optical Band Gap in La Doped Bismuth Titanate with Two Stage Doping

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The wide band gap of complex oxides is one of the major obstacles limiting their use in photovoltaic cells. To tune the band gap of complex oxides, this study examined the effects of chemical/oxygen vacancy doping on $Bi_4Ti_3O_{12}$ based oxides synthesized using a solid reaction method. The structural, optical and electrical properties of the synthesized powers were determined by x-ray diffraction, scanning electron microscopy, ultraviolet-visible spectroscopy, and resistant measurements. Both types of doping, chemical doping and oxygen doping, could affect the tunability of the band gap. On the other hand, the decrease in band gap from oxygen vacancy doping was much more significant in the chemical doped sample than in the sample without chemical doping. Two stage doping, which combined chemical and oxygen vacancy doping, of La doped bismuth titanate reduced the band gap of La doped bismuth titanate from 2.75eV to 1.2eV without breaking symmetry.

Keywords Bismuth titanate; band gap engineering; chemical doping; oxygen vacancy doping

Introduction

Complex oxides are used widely in a range of applications, such as field-effect transistors (FETs) and thin film transistors (TFTs). Recently opto-electronic systems have attracted considerable attention. Among the many classes of materials, complex oxide materials are emerging again as candidates for opto-electronic device applications, such as photovoltaic devices and photo detectors [1–4]. They have a range of useful properties, e.g. ferroelectricity can boost the photoelectric response. By utilizing the spontaneous polarization of ferroelectric oxides, a photovoltaic cell can produce a higher voltage than the band gap energy of the material [5–6]. Moreover, complex oxides are extremely stable and can survive harsh environments, such as high temperature, high humidity and exposure to many hazardous chemicals. On the other hand, most complex oxides have a much wider band gap than the materials commercially available for photovoltaic cells. The wide band gap governs the upper limit of the absorption energy from solar light, and is a major obstacle that limiting the use of these materials as photovoltaic cells [7].

Therefore, the ability to tune the band gap is important for developing highly efficient solar cells and transparent conducting oxides. To tune the band gap of complex oxides, this

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study examined the effects of chemical /oxygen vacancy doping on $Bi_4Ti_3O_{12}$ (BiT)-based oxides synthesized using a simple alloying method. BiT was chosen as the model material because of its attractive properties.

The Aurivillius family is a class of complex bismuth titanate-based oxides that have number of layered perovskite structures [8]. These compounds, $(Bi_2O_2)^{2+}(A_{n\text{-}1}B_nO_{3n+1})^{2-}$, are normally good insulators, which have a dielectric response, and crystal symmetry in some compositions, e.g. BiT can exhibit ferroelectricity [9]. In addition, unlike other type of ferroelectric materials, the electrical and structural properties of Aurivillius phases can be maintained even after extensive chemical and oxygen vacancy doping of the phase owing to its layered structure with alternating Bi_2O_2 and $Bi_2Ti_3O_{10}$ layers.

For these reasons, Aurivillius phases are good candidate materials for solving the wide band gap problem, which is one of the major obstacles that limit photoelectric applications [10]. On the other hand, most attention on BiT-based oxides has been focused on the development of ferroelectric memory. Few studies have examined the optical response and band gap tunability [11].

Fabricating complex transition metal oxides with a tunable band gap without losing the useful ferroelectricity is a longstanding challenge. Density functional theory calculations have attributed the decrease in band gap to an additional Co electronic state just below the conduction band of BiT [12–13]. Recently, superlattice films grown using $LaCoO_3$ and $Bi_4Ti_3O_{12}$ (BiT) can be one approach to systematically lowering the band gap of the materials [12]. In addition, a series of oxygen vacancy doping induced band-gap narrowing and enhanced the visible light activity of bismuth titanate [14–15]. One study reported that oxygen vacancies readily form in the Aurivillius structure without compromising the ferroelectricity [16]. Although both types of doping are effective in reducing the wide band gap of oxides, there are no reports of combining the two methods in bismuth titanate.

To identify a useful route for effectively tailoring the band gap of complex oxides, this study attempted to reduce the optical band gap of the parent material (LBiT) using two methods, chemical doping and oxygen vacancy doping. Using the first method, chemical doping, La and Co doped atoms were substituted into a layered ferroelectric $Bi_4Ti_3O_{12}$ (BiT) to synthesize $(Bi_{3.25}La_{0.75})Ti_3O_{12}$(LBiT) and $(Bi_{3.25}La_{0.75})(CoTi_2)O_{12}$,(Co-LBiT). With the other type of doping, oxygen vacancy doping, two oxygen deficient Aurivillius phases, $(Bi_{3.25}La_{0.75})Ti_3O_{12\text{-}x}$ (LBiT(OD)) and $(Bi_{3.25}La_{0.75})(CoTi_2)O_{12\text{-}x}$,(Co-LBiT(OD)), were synthesized. A series of doped samples were synthesized using a simple solid reaction method without some of state-of-the-art techniques to grow the superlattice structure. These powders were characterized structurally by X-ray diffraction (XRD). Although heavy chemical and oxygen vacancies in oxide materials can break their crystallographic symmetry, all the doped bismuth titanate maintained their original structure, orthorhombic symmetry, owing to the structural uniqueness of the Aurivillius phase [13].

The optical band gaps of the synthesized powers were determined by ultraviolet-visible(UV-Vis) absorption spectroscopy. As a result, the band gap of LBiT could be reduced considerably using the two stage doping method; the measured the optical band gap were reduced from 2.7 eV (LBiT) to below 1.2eV (Co-LBiT(OD)).

Experimental Procedure

To analyze the chemical/oxygen vacancy doping effect on the band gap, bismuth-layered structure-based powders, corresponding to the compositions, $Bi_{3.25}La_{0.75}Ti_3O_{12}$(LBiT), $Bi_{3.25}La_{0.75}CoTi_2O_{12}$(Co-LBiT) and oxygen deficient $Bi_{3.25}La_{0.75}Ti_3O_{12\text{-}x}$(LBiT(OD)),

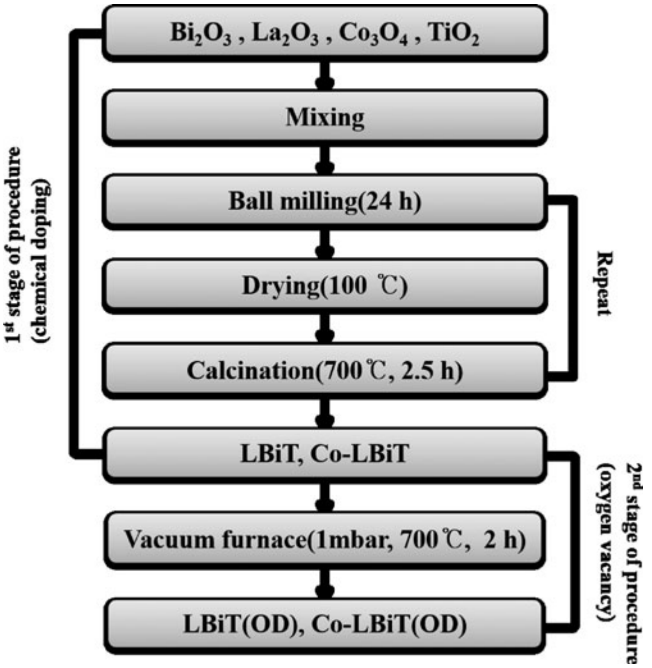

Figure 1. Procedure to synthesize LBiT, Co-LBiT and LBiT(OD), Co-LBiT(OD) powders.

$Bi_{3.25}La_{0.75}CoTi_2O_{12-x}$(Co-LBiT(OD)), were prepared. Figure 1 summarizes the entire procedure.

The samples were synthesized using a solid-state reaction method with the starting binary oxide powders, Bi_2O_3 (99.9%, Kojundo), TiO_2 (99.99%, Kojundo), La_2O_3 (99.99%, Kojundo), and Co_3O_4 (99.9%, Kojundo) as raw materials. The blended powders at the stoichiometric ratio were mixed thoroughly in a ball mill for 24 hours, dried in an oven at 100 °C and calcined at 700 °C for 2.5 hours in air. The resulting calcined powders were milled and calcined again under the same conditions. From the 1st stage of the procedure, LBiT powders with and without cobalt doping were synthesized and amount of Co atoms were substituted for Ti atoms.

For the oxygen deficient phase, oxygen vacancies were generated in the LBiT and Co-LBiT samples by a heat treatment in a vacuum furnace at a partial pressure of 1 mbar at 700 °C for 2 hours in the 2nd stage of the procedure. As a result, oxygen deficient phases, LBiT(OD), Co-LBiT(OD), were obtained from LBIT and Co-LBiT, respectively.

The samples were characterized structurally by XRD (Rigaku, D/MAX 2200) using Cu K_α radiation over the 20 to 80° 2θ with an angular step of 0.02°/min. The microstructure of synthesized powers was examined by scanning electron microscopy (SEM, Hitachi, S-4700). To estimate the optical band-gap, the optical properties were measured using a UV-Vis spectrometer (Agilent, 8453). The resistance of the sample was measured using a multi tester.

Results and Discussion

Figure 2 shows that XRD patterns of the cobalt free LBiT, Co-LBiT, oxygen deficient LBiT(OD) and Co-LBiT(OD). The XRD patterns were well matched with that reported for

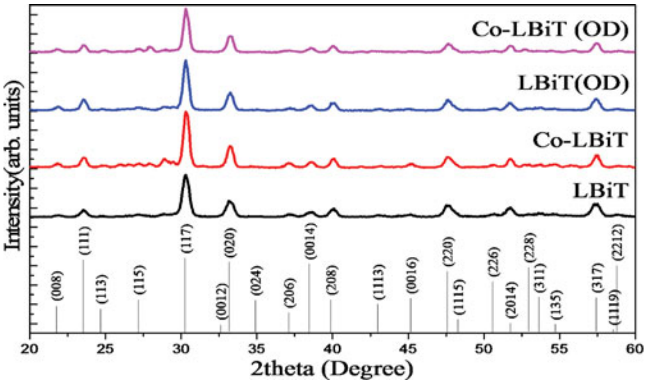

Figure 2. XRD patterns of LBiT, Co-LBiT and LBiT(OD), Co-LBiT(OD) powders. The vertical lines indicate the position of ICSD No. 150091.

$Bi_{3.25}La_{0.75}Ti_3O_{12}$ with an orthorhombic structure (ICSD No. 150091). The XRD patterns were in agreement with the previously reported LBiT structures, which had been grown using, different growth methods such as sol-gel, hydrothermal and complex polymerization method [15, 17–18]. This suggests that the location of the peaks with orthorhombic symmetry remain unchanged for all samples, indicating that the Aurivillius structure had been maintained without breaking symmetry.

XRD confirmed that Co and oxygen vacancies were incorporated successfully into the LBiT unit cell, but excess Co atoms formed a negligible amount of a secondary phase. Co naturally develops a cobalt oxide secondary phase in heavily cobalt-doped samples. For example, a cobalt oxide secondary phase was detected even in the superlattice films, in which each layer was grown separately from the LCO and BIT ceramic targets. On the other hand, the secondary phase did not reduce the band gap in the bismuth titanate matrix.

The peak broadening of LBiT, Co-LBiT, LBiT(OD), and Co-LBiT(OD) was similar in the XRD pattern. This suggests that the mean powder sizes of all the samples are almost identical to each other based on Fig. 2.

Figure 3 shows SEM images of the as-calcined samples. Fig. 3-(A), (B), (C), (D) show the microstructures of the LBiT and Co-LBiT and LBiT(OD) and Co-LBiT(OD). The specimens consisted of plate like grains with a random orientation of plate faces. Plate-like grain formation was reported to be a typical characteristic of bismuth layer-structured ferroelectrics because they have a highly anisotropic crystal structure. The microstructure is dominated by the presence of polygonal edges grains. As expected from XRD, the grain size and shape in a series of the samples were almost identical to each other according to SEM.

UV-vis absorption spectroscopy was used to determine band gap of samples. Figure 4 shows the optical bandgap (E_g) of the samples (LBiT, Co-LBiT, LBiT(OD), and Co-LBiT(OD)) measured from the UV-vis absorbance spectra at wavelengths from 200 to 800nm. The E_g values of the samples were evaluated extrapolating the linear portion of the curve or tail towards the x-axis [15, 19–20].

Consequently, the optical band gap of cobalt doped LBiT, Co-LBiT powder was decreased dramatically to as low as 2.0 eV compared to the measured optical band gap of the cobalt free LBiT powder (2.75 eV), as shown in Fig. 4. The secondary phase did

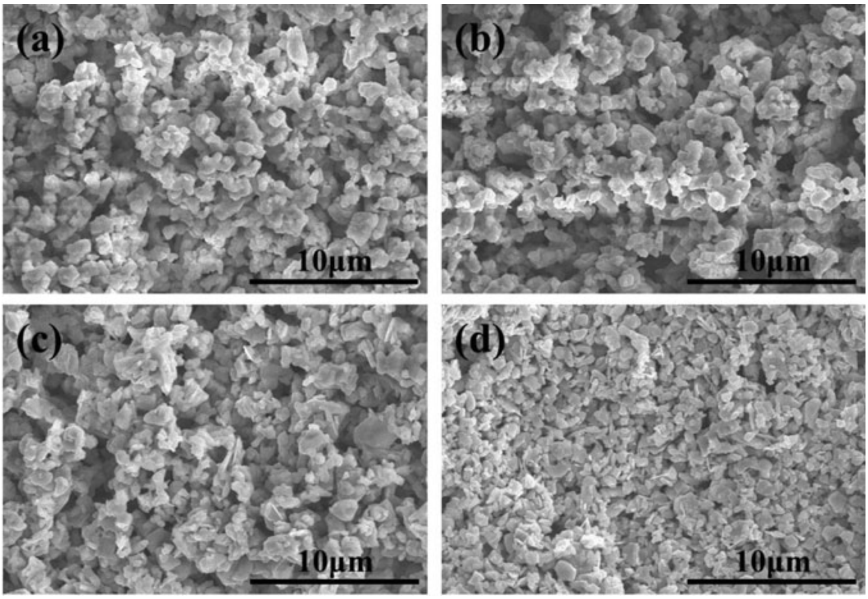

Figure 3. SEM images of (a) LBiT, (b) Co-LBiT, (c) LBiT(OD), (d) Co-LBiT(OD).

not affect the optical bandgap. The color of cobalt free LBiT powders was yellowish, whereas the Co doped BiT powders showed a darker color due to the increased absorption in the visible range. These results suggest that the optical band gap could be reduced and controlled by Co-doping.

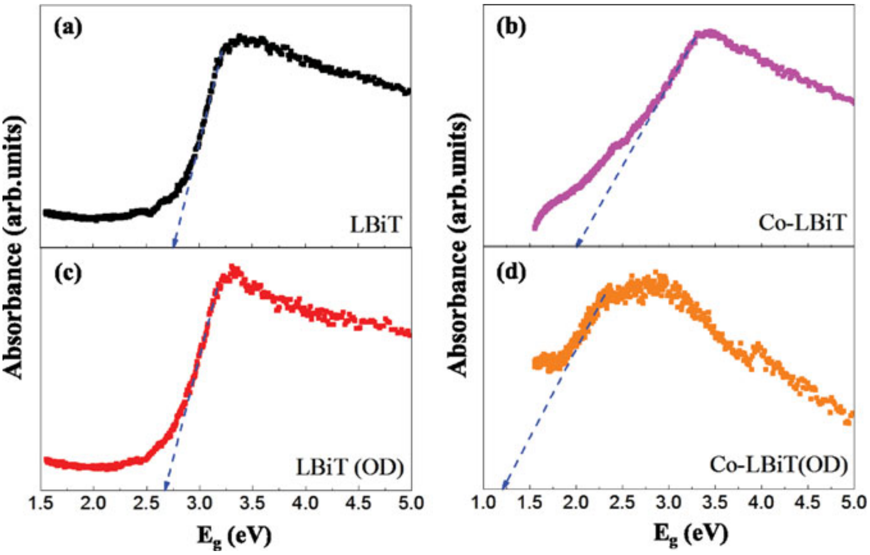

Figure 4. UV-vis absorbance spectra of the LBiT-based powders, (a) LBiT, (b) Co-LBiT, (c) LBiT(OD), (d) Co-LBiT(OD).The extrapolation lines (dashed lines) indicates the optical band gap. The E_g value can be obtained by extrapolating the linear segments of the curves towards the x-axis.

Even if the materials had the same chemical ratio, the reported optical band gap energy differed according to the materials (film (∼3 eV), powder (below 3 eV)), synthesis method and synthesis conditions (e.g. calcination temperature).The same synthesis conditions were used during the entire procedure to exclude the extrinsic parameters, which can affect the band gap of the materials. In addition, the grain size and shape were identical in all samples according to XRD and SEM. The measured optical band gaps of the LBiT powder (2.75 eV) grown in the present study agreed well with the data reported for the powder form [13, 15].

The oxygen vacancy-generated LBiT and Co-LBiT powders after a heat treatment in a vacuum furnace were examined by UV-vis spectroscopy. The optical band gap of LBiT(OD) and Co-LBiT(OD) was 2.6 eV and 1.2 eV, respectively. The oxygen vacancies generated in the samples resulted in a significant decrease in band-gap. Oxygen vacancies induced band-gap narrowing and enhanced visible light photocatalytic activity in ZnO [21]. Other studies have shown that a high concentration of oxygen vacancies in ZnO leads to an enhancement of the visible light absorption capability and the observed band gap narrowing is closely related to the oxygen vacancy concentrations, e.g. ZnO with the highest oxygen vacancy concentrations has the best visible light response. Accordingly, oxygen vacancies can narrow the band gap instead of just forming active centers or trap centers [22]. In addition, oxygen vacancies were reported to cause some changes in the electronic structure of TNTs/N2 aggregation and extend the Fermi level to the conduction band [23]. For example, in a TiO_2 crystal, the Fermi surface of the total density of states (TDOS) extended into the conduction band, which led to a decrease in band gap. According to these calculations, the band gap of the TiO_2 with oxygen vacancies was reduced by approximately 0.176 eV. Without doping, oxygen vacancies exert an important influence on the optical properties of TiO_2 crystals and are responsible for the large improvement in photocatalytic efficiency.

The LBiT(OD) sample showed a lower bandgap than the LBiT sample, albeit not large, whereas the Co-LBiT(OD) sample showed remarkably reduced optical band gap compared to the LBiT(OD) sample. The mechanism for huge difference in band gap between the cobalt free and cobalt doped oxygen deficient phases will require further study. Nevertheless, the dramatically narrowing of the band gap in Co-LBiT(OD) cannot be attributed to experimental error. As shown in figure 5, Co-LBiT(OD) exhibited conducting behavior due to band gap narrowing, whereas the other three sample, LBiT(OD), LBiT, Co-LBiT showed

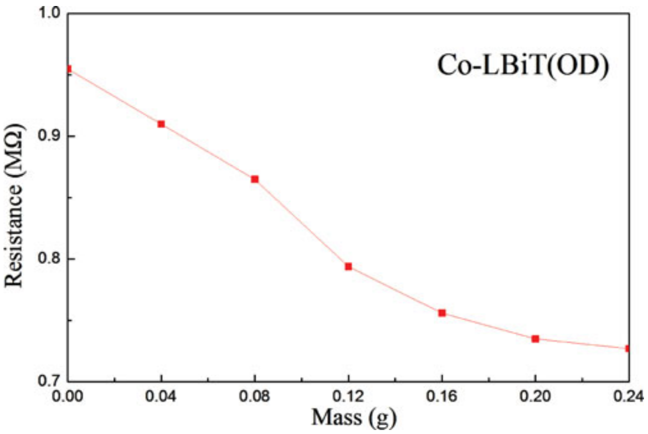

Figure 5. Resistance of dispersive Co-LBiT(OD) with a mass of 0 to 0.24 g in distilled water.

completely insulating behavior. The resistance of the dispersive Co-LBiT(OD) powders in distilled water (16ml) was reduced sharply from 0.91 to 0.727 MΩ unlike the other samples. The Co-LBiT(OD) sample was characterized as an electric conductor whereas the other samples were classified as insulators.

Conclusion

Chemical and oxygen vacancy doping of LBiT was performed in an attempt to control the band gap. The substitution of a Co atom to Ti was used for chemical doping, and heat treatment in a vacuum furnace was used for oxygen vacancy doping of LBiT and Co-LBiT powders. Cobalt-doped powder had a band gap of approximately 2 eV, which is much lower than that of the LBiT powder, ∼2.75 eV. Additional oxygen vacancy doping of LBiT, Co-LBiT could give rise to further tenability; the band gap of LBiT(OD) and Co-LBiT(OD) were 2.6 eV and ∼1.2 eV, respectively. Interestingly, although heat treatment was used to generate oxygen vacancies in LBIT and Co-LBiT were exactly same, the decrease in band gap in the Co-LBiT(OD) sample was much larger than that of the oxygen deficient sample without cobalt doping, LBIT (OD). The Co-LBiT(OD) samples produced by chemical and oxygen vacancy doping showed a significantly lower optical band gap than the other samples. Control of the band gap chemical and oxygen vacancy doping can be applied to other complex oxides materials and provides a new tool for manipulating oxide optoelectronics.

Acknowledgment

This study was supported by the Human Resources Development program (No. 20124030200010) of the Korea Institute of Energy Technology Evaluation and Planning (KETEP) grant funded by the Korea government Ministry of Trade, Industry and Energy and Basic Science Research Program through the National Research Foundation of Korea(NRF) funded by the Ministry of Science, ICT & Future Planning (No. 2013005417).

References

[1] Choi, T., Lee, S., Choi, Y. J., Kiryukhin, V., & Cheong, S.-W. (2009). *Science*, *324*, 63.

[2] Yang, S. Y., Seidel, J., Byrnes, S. J., Shafer, P., Yang, C.-H., Rossell, M. D., Yu, P., Chu, Y. -H., Scott, J. F., Ager, J. W., Martin, L. W., & Ramesh, R. (2010). *Nat. Nanotech.*, *5*, 143.

[3] Huang, H. (2010). *Nat Photon*, *4*, 134–135.

[4] Irvin, P., Ma, Y., Bogorin, D. F., Cen, C., Bark, C. W., Folkman, C. M., Eom, C.-B., & LevyJ.. (2010) *Nat. Photon.*, *4*, 849–852.

[5] Yuan, Y., Reece, T. J., Sharma, P., Poddar, S., Ducharme, S., Gruverman, A., Yang, Y., & Huang, J.. (2011) *Nat. Mater.*, *10*, 296–302.

[6] Seidel, J., Fu, D., Yang, S. Y., Alarcon-Llado, E., Wu, J., Ramesh, R., & Ager, J. W. (2011). *Phys. Rev. Lett.*, *107*, 12, 126805.

[7] Jia, C., Chen, Y., & Zhang, W. F. (2009). *J. Appl. Phys.*, *105*, 113108.

[8] Aurivillius, B. (1949). *Arkiv. Kemi. 1*, 58, 499–512.

[9] Subbarao, E. C. *Phys. Rev.*, *122*, 3, 804–807 (1961).

[10] Singh, D. J., Seo, S. S. A., & Lee, H. N. (2010). *Phys. Rev. B.*, *82*, 180103.

[11] Ehara, S., Muramatsu, K., Shimazu, M., Tanaka, J., Tsukioka, M., Mori, Y., Hattori, T., & Tamura, H. (1981). *Jpn. J. Appl. Phys.*, *20*, 877.

[12] Choi, W. S., Lee, H. N. (2012). *Appl. Phys. Lett.*, *100*, 13, 132903.

[13] Choi, W. S., Chisholm, M. F., Singh, D. J., Choi, T., Jellison, G. E., & Lee, H. N. (2012). *Nat. Comm.*, *3*, 689.

[14] Skorikov, V. M., Zakharov, I. S., Volkov, V. V., Spirin, E. A., & Umrikhin, V. V. (2001). *Inorganic Materials.*, *37*, 11, 1149–1154.

[15] Oliveira, R. C., Sczancoski, J. C., Aguiar, E. C., Espinosa, J. W. M., Varela, J. A., Pizani, P. S., Longo., E., & Cavalcante, L. S. (2009). *J. Alloys Compd.*, *478*, 661.

[16] Lee, H. N., Hesse, D., Zakharov, N., & Gösele, U. (2002). *Science.*, *296*, 2006.

[17] Hashimoto, T., & Moriwake, H. (2008). *Phys. Rev. B. 78*, 092106.

[18] Siriprapa, Pasinee, Watcharapasorn, Anucha, & Jiansirisomboon, Sukanda (2012). *Nanoscale Research Letter.*, *7*, 42.

[19] Elshabini-Raid, A. A. R., & Barlow, F. D. (1998). *Thin Film Technology Handbook*, McGraw-Hill, New York, NY, USA.

[20] Wood, D. L., Tauc., J. (1972). *Phys. Rev. B.*, *5*, 3144.

[21] Vanheusden, K., Seager, C. H., Warren, W. L., Tallant, D. R., & Voigt, J. A. (1996). *Appl. Phys. Lett.*, *68*, 403.

[22] Wang, J., Wang, Z., Huang, B., Ma, Y., Liu, Y., Qin, X., Zhang, X., & Dai, Y. (2012). *ACS Appl Mater Inter.*, *4*, 8, 4024–4030.

[23] Liu, Feila, Lu, Lu, Xiao, Peng, He, Huichao, Qiao, Lei, & Zhang, Yunhuai (2012). *Bulletin of the Korean Chemical Society.*, *33*, 7, 2255–2259.